

We thank the reviewers for their careful examination of our manuscript, and the insightful comments which have helped to improve our manuscript substantially. Below we provided a point-to-point response to the reviewers' comment, where the reviewers' comments are in black, and our responses are in blue.

Reviewer #2

Lin et al. present an interesting analysis of the contributions of solid fuel combustion for heating to PM levels in Dublin. PMF ME-2 modeling is applied to observations from an ACSM using two approaches (conventional "a" value and limits approaches) to assess differences and uncertainties in resulting source apportionments. Both the study findings re: the importance of solid fuel combustion as an evening PM source and more methodological findings re: the ME-2 approaches will be of interest to AMT readers. I have a number of comments for the authors to consider:

Response: We thank the reviewer for the positive comment. See below for a point-to-point response to the comment.

Line 23: It would be better here to refer to normalized peak intensities.

Response: Now referred. It now reads, "...the peak intensities obtained at specific m/z values in the normalized mass spectra were not constant..."

Line 25: It would be better to refer to Positive Matrix Factorization (PMF) analysis using the Multilinear Engine algorithm (ME-2)

Response: Now referred. It now reads, "Using the OA mass spectra of peat, wood, and coal as anchoring profiles and the variation of individual m/z values for the upper/lower limits (the limits approach) in the Positive Matrix Factorization (PMF) analysis with the Multilinear Engine algorithm (ME-2), the respective contributions of these fuels to ambient sub-micron aerosols during a winter period in Dublin were evaluated and compared with the conventional a value approach."

It would be helpful for the authors to provide more detailed information about the fuels burned. For example, there are many types of wood. What wood type(s) are burned in Dublin and what type(s) were used in stove testing? How about peat?

Response: We have now provided details about the fuels burned in the Method Section. It now reads, "Five fuel types were tested including wood, peat, smoky coal, biomass briquettes, and smokeless coal (Table 1). Specifically, wood logs were cut from softwood grown in Ireland; peat was obtained from the peatland in Leitrim, Ireland, and was naturally dried before testing; smoky coal (Silesia, Poland) were purchased from local retail outlets (Trubetskaya et al., 2021); biomass briquettes and smokeless coal (i.e., Ecobrite ovoids) were manufactured at Arigna Fuels (Carrick on Shannon, Ireland)."

Line 87: chloride in biomass burning PM is often present as KCl which vaporizes slowly on the AMS vaporizer, requiring a non-standard treatment of the AMS data. See, for example, the SI in Lee et al. (2010) *Aerosol Sci. Tech.*; doi: 10.1080/02786826.2010.499884. How was this issue accounted for in ACSM processing for the Dublin study?

Response: In this study, we focused on the mass spectral profiles of organic aerosol, and the issue of the slow vaporization of KCl was not accounted for in ACSM processing. In the method section, we pointed out such concerns, it now reads, "Note that chloride in the aerosol emission from biomass burning is

often present as KCl which vaporizes slowly at 600 °C, requiring a non-standard treatment of the ACSM chloride data (Lee et al., 2010). In this study, we focused on the mass spectral profiles of OA emissions, and the slow vaporization issue was not accounted for (Lee et al., 2010).”

I would like to see a more robust analysis of the comparison between the study site PM₁ data and the EPA Ireland PM_{2.5} site data. Only an R-squared value is given. I suggest adding a scatter plot to SI and discussing not just the correlation but also the slope and intercept of the relationship between the PM₁ and PM_{2.5} measurements. High correlation does not necessarily imply similar PM values at the two sites, just similar temporal variability. Are there other Dublin PM data that could be used to look beyond two locations (e.g., Purple Air monitors) to make a more general assessment of urban PM spatial variability?

Response: We have now added a scatter plot to SI. Slope and intercept of the relationship between PM₁ and PM_{2.5} are also provided (See Figure R4 above or Figure S1 in the revised SI). It now reads, “The slope of 0.74 for the linear relationship between PM₁ and PM_{2.5} suggests PM₁ on average accounts for 74% of PM_{2.5}. However, during pollution events, the values of PM₁ and PM_{2.5} are very similar, indicating most PM are in the submicron size ranges.”

For the current sampling period (i.e., winter of 2016-2017), other Dublin PM data are not available and, thus, we will not extend the discussion. However, during the heating season in 2018 as shown in Lin et al. (2020), PM₁ (ACSM+AE33) at a third sampling site (i.e., the roadside in the Dublin city center) also shows an elevated concentration at a similar level as found at the two sampling sites as presented in this study, suggesting heating emissions impact a large area in Dublin.

m/z 60 in the AMS comes from multiple anhydrosugars, including levoglucosan, mannosan, and galactosan – and probably from other similarly structured molecules, too (see, for example, the Lee et al. (2010) paper). This should be stated in the manuscript. Levoglucosan is produced during combustion of cellulose. Mannosan and galactosan come from pyrolysis of hemi-cellulose. The authors should also point, therefore, to the combined fuel content of cellulose and hemi-cellulose, in discussing relationships between fuel and m/z 60.

Response: We thank the reviewer for pointing this out. We have now pointed out the relationship between the fuel content of cellulose/hemicellulose and the observed signal at m/z 60. It now reads, “Mass fragment at m/z 60 (mostly from the C₂H₄O₂⁺) is due to the fragmentation of anhydrosugars (e.g., levoglucosan, mannosan, and galactosan from the combustion of cellulose/hemicellulose; (Lee et al., 2010)) in the ACSM, and it is, therefore, commonly used as a marker for biomass burning in the AMS/ACSM studies (Cubison et al., 2011; Lee et al., 2010). Therefore, the differences in the content of cellulose/hemicellulose in the test fuels partly contribute to the differences in ion intensity at m/z 60 in ACSM.”

Line 173: the text in this line needs to be corrected. I think an extra “m/z” was inadvertently included.

Response: Corrected. “m/z” is now removed.

Line 175: Please define your term **difference ratio** mathematically in the text.

Response: It is now defined, it reads, “...calculated by $(f_{m/z, \text{stove y}} - f_{m/z, \text{stove x}}) / f_{m/z, \text{stove x}}$ where $f_{m/z}$ represents the fraction of the measured m/z to the total organic signal, while stove y represents the Ecodesign or the Boiler stove, and stove x represents the conventional stove; Fig. S3 and S4)...”

2nd half of P. 6: Discussions here about reduced fractional abundance of certain ions are oversimplified. Since f_{60} , for example, refers to the fractional abundance of m/z_{60} , a reduction in f_{60} is expected when the amount of its solid fuel precursors (cellulose + hemicellulose +?) decreases *more than* the amount of precursors for other m/z ions observed in the AMS. The same is true for the fractional abundance of PAH-related fragments.

Response: We agree that reduced f_{60} was likely due to the relatively large reduction of e.g., cellulose/hemicellulose content in the fuel compared to other precursors since the mass spectra are normalized. In the text, it now reads, “The reduced f_{60} in the normalized mass spectra for smoky/smokeless coal is likely due to the breakdown of e.g., cellulose during coal formation over millions of years (Höök, 2012), resulting in a relatively low content of cellulose, while accumulating other carbon-rich content, leading to the observed ions at other m/z 's. As a comparison, the large contribution from the fragments at m/z 77, 91, and 115 suggests a high content of aromatic/polycyclic aromatic hydrocarbon (PAH) compounds in the smoky coal burning emissions.”

The diurnal cycle of secondary inorganic species (ammonium, sulfate, nitrate) in the ACSM obs and the source profiles is interesting. Can the authors say more about the origin of these secondary components? Does a combination of ammonia emissions from the solid fuel combustion and lower evening temperatures drive up ammonium nitrate formation in the evening? How much primary sulfate was observed in the stove emissions?

Response: We thank the reviewer for pointing this out. We have now discussed more on the secondary inorganic species (i.e., ammonium, sulfate, nitrate) in the revised manuscript. Specifically, the diurnal pattern of ammonium, nitrate, and sulfate all showed peaks at the same evening hours (20:00-22:00) with the BC (Figure R1 below or Figure S6 in the revised SI), suggesting they may also be related to heating emissions combined with low temperatures. In the stove emission, sulfate was found to contribute to <1% of PM_{10} for wood burning combustions but the fraction of sulfate was up to 21% of PM_{10} for smokeless coal, reflecting the higher content of sulfur in the raw fuel (Trubetskaya et al., 2021). However, since ammonia data are not available for both the combustion and ambient studies, we tend not to discuss more on the ammonium nitrate formation, which will be the focus of future studies.

It now reads, “...the diurnal pattern of ammonium, nitrate, and sulfate all showed peaks at the same evening hours with the BC (Fig. 4a), suggesting they may also be related to heating emissions coupled with low temperatures in the evening (Fig. S6). Sulfate was likely associated with the primary emissions from solid fuel combustion (Trubetskaya et al., 2021) given that, in the stove emission, sulfate was found to contribute to <1% of PM_{10} for wood burning but the fraction of sulfate was up to 21% of PM_{10} for smokeless coal burning, reflecting the higher content of sulfur in the raw fuel (Trubetskaya et al., 2021). This is consistent with our previous study (Lin et al., 2019), where we demonstrated that sulfate, nitrate, and ammonium can be locally emitted/formed, as well as regionally transported, through the comparison of the ACSM measurement at the same Dublin sampling site and at Carnsore Point, a regional background site...”

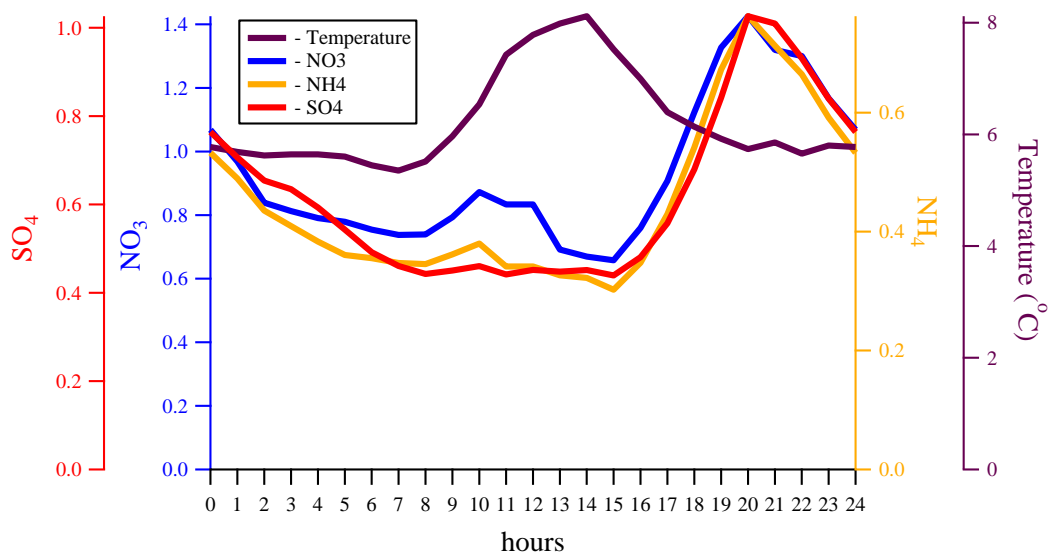


Figure R1. Zoomed-in plot of the averaged diurnal cycle of sulfate (SO₄), ammonium (NH₄), and nitrate (NO₃) in µg m⁻³, as well as the temperature (°C) over the entire sampling period.

page 8: In addition to the daily breakdown of OA contributors, please provide the breakdown for the evening period when stove emissions dominate.

Response: The original Fig. 5f and 5g show the relative contribution of the resolved factors during the evening hours (20:00-23:00) when stove emissions dominate. However, it was not clear in the original text. In the revised text, we have now clarified this. It now reads "...both approaches showed peat burning being the largest OA factor (39% (Fig. 5f) vs 41% (Fig. 5g)), followed by HOA (24 vs 25%), OOA (20 vs 18%), wood (14% vs 11%), and coal (4% vs 5%) during the evening hours (20:00-23:00) when stove emissions dominate..."

Lines 272-273: Please add a citation to the statement regarding CO₂ capture during biomass growth.

Response: Added. It now reads, "...through photosynthesis during growing as is released when biomass is burned (Marland, 2010)..."

Lines 283-284: I think the authors mean to say "Therefore, extending the ban *to* the use of peat and wood...." As written it sounds as if they are referring to extending an existing ban on peat and wood burning when I think they mean to suggest extending the current ban on burning smoky coal to also forbid peat and wood burning.

Response: Thank you for pointing this out. It is now changed to "...Therefore, extending the ban to the use of peat and wood..."

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